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PREPARATION AND STUDY OF NEWLY MODIFIED RUBBER COMPOUNDS WITH THE ADDITION OF NATURAL ZEOLITES

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ABSTRACT: The present work deals with the preparation and study of modified polymer compounds with the addition of nanoadditives on the base of natural zeolites. Zeolites form a group of aluminosilicate nanoporous materials, which can be used in the role of fillers in the polymer materials. Prepared modified polymer compounds were characterized by methods of thermal analysis and their vulcanization performance and physical-mechanical properties of vulcanizates were measured. Obtained values were compared to the values of commercially used polymer materials with the original composition [1,2].

KEY WORDS: zeolites, nano-additives, polymer materials, physical-mechanical properties

1. INTRODUCTION

Natural zeolites form a group of hydrated aluminosilicates with the porous structure. The best known type of zeolite is called clinoptilolite. Its structure is based on three dimensional framework composed of tetrahedral SiO_4 and AlO_4 units, which are connected by shared oxygen atoms. The special structure of zeolite has lots of practical applications as an ion-exchange, adsorbent, material for reversible hydration and dehydration, and also as a nanofiller in the polymer materials [3].

The application of inorganic materials in organic polymers is one of the usual ways to improve physical-mechanical properties of polymer. Composite materials generally display better properties than pure and homogeneous materials. Changes are possible to be observed at very low concentration of inorganic component in the polymers [4].

Present paper deals with the preparation of modified rubber compounds in the presence of nanoadditive on the base of clinoptilolite and gives the information on their rheology, vulcanization performance and physical-mechanical properties.

2. EXPERIMENT

2.1 Preparation of modified rubber compounds samples

The nanofiller of natural zeolite used in the experiments was obtained from region of Majerovce SR. It was ground and fraction of 0 – 0.2 mm was selected.

The rubber compounds were prepared by mixing in laboratory mixer Plastograf-Brabender in two steps (STN 62 1425) [5]. Individual amounts of mixed components and used conditions are given in Table 1. Sample Zo-1 – modified rubber compound with the substitution of all amount of filler clinoptilolite. Sample Zo-1/2 – modified rubber compound with the substitution of 1/2 amount of filler clinoptilolite.

Tab. 1: Conditions and amounts of components

I. step of mixing			
Temperature			140 °C
Time of mixing			8 minutes
Additives / sample	Standard [g]	Zo-1 [g]	Zo-1/2 [g]
Natural rubber	59.400	59.400	59.400
Activator of vulcanization (ZnO)	2.734	2.734	2.734
Filler (carbon black)	5.940	-	2.9700
Filler (zeolite)	-	5.940	2.9700
Accelerator of vulcanization (CBS)	0.892	0.892	0.892
Time of stay			24 hours
II. step of mixing			
Temperature			110 °C
Time of mixing			6 minutes
Addition of vulcanization reagent (sulfur)			1.067
Time of stay			24 hours

2.2 Methods and equipments

Selected samples of newly prepared modified rubber compounds were studied by methods of thermal analysis – DTA, TG, DSC. Differential thermal analysis and Thermogravimetry were measured by use of Derivatograph (Paulik, Paulik, and Erdey, MOM, Budapest), in the temperature range of 40 °C - 900 °C with heating rate of 10 °C.min^{-1}. From thermograms DTA and TG the dependence of $\Delta T = f(T)$ and $\Delta m = f(T)$ was obtained.

For DSC study we used Differential scanning calorimeter PYRIS Diamond DSC Perkin Elmer. Measurements were provided in the temperature range of 30 °C - 250 °C by experimental conditions: scanning rate of 10 °C.min^{-1}, calibration of temperature and enthalpy was performed with the use of pure In.

Rheological and vulcanization performances (M_L, M_H, t_S, t_{90}, R_V) of prepared rubber compounds with the addition of nanofiller – clinoptilolite were tested and physical-mechanical properties of vulcanized rubber were studied.

Determination of vulcanization performance was made by vulcameter Monsanto 100 by STN 62 1416 at the temperature 150 °C during 60 min. For determination of physical-mechanical properties of vulcanized rubber – stress-strain properties (tensile strength, modulus 300, tensibility) we used instrument INSTRON at the temperature 23 ± 2 °C by STN 62 1436 (ISO 37). Hardness was measured by hardness tester IRHD by STN 62 1433 at the temperature 23 ± 2 °C [5].

Values of prepared modified rubber compounds were compared to the standard (commercial rubber compound).

3. RESULTS AND DISCUSION

3.1 Thermal properties of modified rubber compounds

From results of thermal measurements given in Fig. 1-3 follows a simillarity of thermogram in the case of rubber compound Zo-1/2 with the thermogram of standard. Thermal decomposition of all studied rubber compounds was observed in the temperature range of cca 300 °C - 700 °C. In the case of compound Zo-1 addition of zeolite nanofiller caused changes in the shape of DTA curve – thermal decomposition realized in one step.

In the DSC thermogram (Fig. 4) of the modified rubber compounds with zeolite nanofiller we can see one exotherm in the temperature range of 150 °C - 190 °C belonging to the cure process.

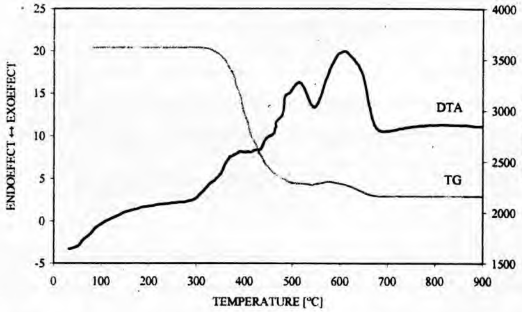

Fig. 1: DTA-TG standard rubber compound

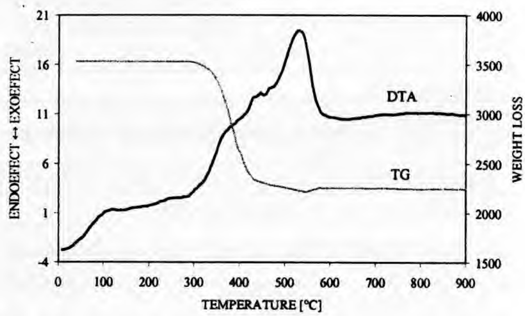

Fig. 2: DTA-TG of rubber compound Zo-1

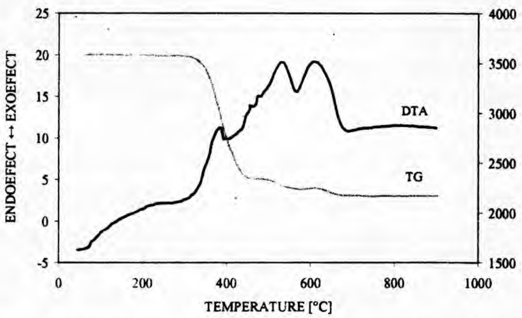

Fig. 3: DTA-TG of rubber compound Zo-1/2

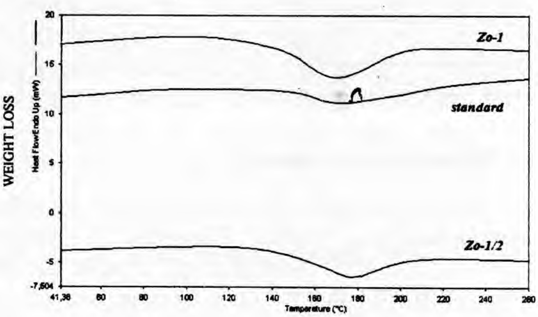

Fig. 4: DSC of rubber compounds

3.2 Rheology and vulcanization performance of modified rubber compounds

The results of measurements are given in Tab. 2 and in Fig. 5-6.

Tab. 2: Rheology and vulcanization performance of compounds

Sample	M_L [N.m]	M_H [N.m]	t_S [min]	t_{90} [min]	R_V [min^{-1}]
standard	5.0	45.0	1.5	3.5	50.0
Z_0 - 1	4.0	38.0	5.5	7.5	50.0
Z_0 – 1/2	8.0	46.0	2.5	4.5	50.0

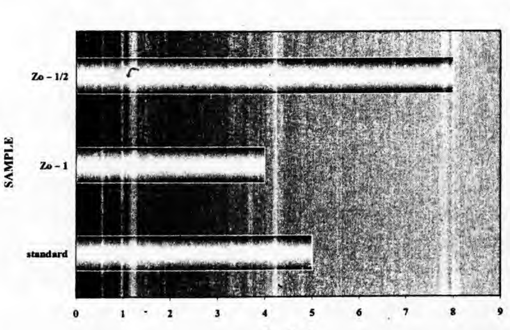

Fig. 5: Initial torgue

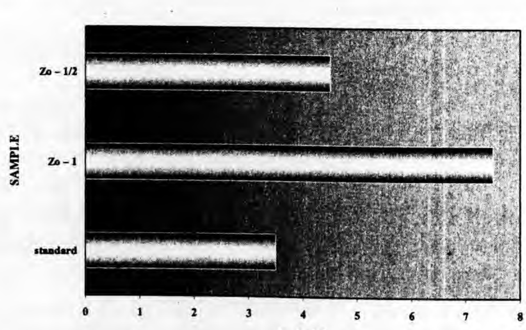

Fig. 6: Optimum of vulcanization

3.3 Physical-mechanical properties of vulcanized rubber

The results of measurements are given in the Tab. 3 and in Fig. 7-8.

Tab. 3: Physical-mechanical properties of compounds

Sample	Tensile strength [MPa]	Modulus 300 [MPa]	Elongation [%]	Hardness [IRHD]
standard	13.17	5.77	685	47.6
Z_0 - 1	11.12	3.91	854	42.3
Z_0 - 1/2	13.65	5.29	774	44.0

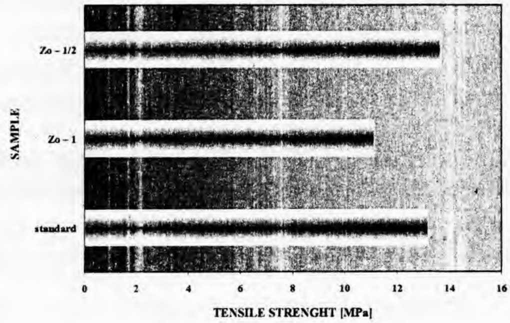

Fig. 7: Tensile strength

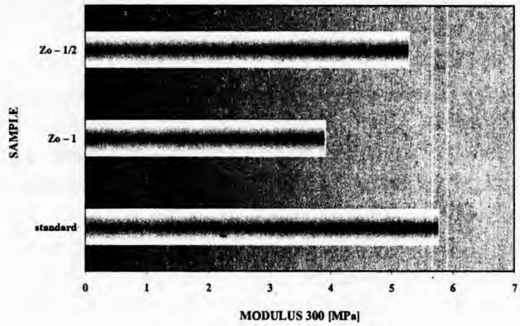

Fig. 8: Modulus 300

Obtained vulcanization performance of rubber compound and physical-mechanical properties of modified vulcanized rubber are comparable to properties of standard commercial rubber compound.

4. CONCLUSION

From study of properties of modified rubber compounds with the addition of natural zeolite nanofiller follows, that natural zeolite – clinoptilolite may be used for the application in rubber compounds improving the physical-mechanical properties.

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